

Self-assembled guanine ribbons as wide-bandgap semiconductors

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Abstract

We present a first principle study about the stability and the electronic properties of a new biomolecular solid-state material, obtained by the self-assembling of guanine (G) molecules. We consider hydrogen-bonded planar ribbons in isolated and stacked configurations. These aggregates present electronic properties similar to inorganic wide-bandgap semiconductors. The formation of Bloch-type orbitals is observed along the stacking direction, while it is negligible in the ribbon plane. Global band-like conduction may be affected by a dipole-field which spontaneously arises along the ribbon axis. Our results indicate that G-ribbon assemblies are promising materials for biomolecular nanodevices, consistently with recent experimental results.

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The possibility that biomolecules may conduct current is intriguing in the development of molecular electronics. In particular, because of their sequence-specific properties, DNA molecules and their derivatives are attractive for nanometer scale electronics, where their self-assembling capability might be used to wire electronic-materials in a programmable way [1], as well as to form novel conducting materials [2, 3, 4].

Indeed, in recent experiments [3, 4], a semiconducting behavior was displayed by a device constituted of a metallic nanogate filled with a dried solution of a lipophilic deoxyguanosine derivative. This material is composed of hydrogen-bonded planar ribbons, which tend to stack and form solid-state fibers. On a scale of ~ 100 nm, the ribbons self-organize in ordered structures, giving rise to a film of nanocrystalline character [3, 4, 5]. The results of transport and photocurrent experiments identify different regimes, depending on the width (L) of the nanogate: when $L \sim 100 - 200$ nm, few nanocrystals are present between the electrodes and the I-V characteristics present the typical metal-semiconductor-metal behavior; on the contrary, when the gap is reduced ($L < 100$ nm), a single crystal is trapped between electrodes, and the device acts as a rectifying diode. Two concurrent mechanisms have been proposed to explain electron transport in such devices: band-like conduction within the single crystals, and incoherent hopping among neighboring grains. Band conduction and hopping mechanism have been also invoked to describe charge migration in other guanine-rich systems (e.g. G-quartets) or poly(dG)-poly(dC) DNA [2, 6, 7, 8, 9]; however, no conclusive agreement was reached so far in this respect.

In this paper, we present a first principle study of the electronic and conduction properties of self-assembled guanine ribbons: using an extended-solid approach, we analyze the effects of H-bonding and π - π coupling, that control the microscopic interactions along the ribbon axis and along the stacking direction, respectively. Our method is based on *ab-initio* molecular dynamics simulations: we performed total energy and force calculations, optimizing at the same time the atomic positions and the single-particle electronic wave-functions, according to the Car-Parrinello approach [10]. The electronic structure is described within the Density Functional Theory (DFT) [11]; Generalized Gradient Approximation (BLYP-GGA) [12] is applied in exchange-correlation functional to allow an accurate description of H-bonding. The atomic potentials are described by *ab-initio* soft pseudopotentials in the Troullier-Martins [13] formulation. The electronic wave functions are expanded in a plane-wave basis with an energy cutoff of 50 Ry.

With respect to real deoxyguanosine ribbons, our model leaves out the sugar (deoxyribose) and the attached paraffinic chains, because they are not involved in transport phenomena [14, 15]. Since guanine constitutes the building block of the ribbon aggregates, we first study the geometry and the electronic structure of the isolated molecule (see Figure 1, inset). Our method provides an accurate description of the structural parameters: bond lengths and angles are reproduced with an error smaller than 2% with respect to X-ray experimental data [16]. The total charge density has a highly asymmetric distribution, which induces a net dipole ($|\vec{\mu}| = 7$ D) oriented as shown in the inset of Figure 1. The analysis of the electronic structure reveals σ and π electron states. The out-of-plane nature of π orbitals, in particular of the HOMO (Fig. 2a) and of the LUMO, may control the interactions in the stacking direction.

To simulate extended ribbons, we assembled coplanar G molecules according to the experimental geometry [5]. By optimizing the structure of an isolated G dimer, we obtained the intermolecular distance. We used this value to fix the periodicity of the extended structures, whose geometry was also optimized. The periodicity of the ribbons (1.1nm) is in good agreement with the experimental data (1.2nm). The model ribbons (Fig. 1) are 1D planar wires of guanines connected by a H-bond network. The donor-acceptor distances ($\text{NH}\cdots\text{N}=2.9$ Å, $\text{NH}\cdots\text{O}=2.8$ Å) are consistent with previous theoretical results for similar systems (e.g. DNA base-pairs) [17].

H-bonding is a weak interaction, not capable of modifying the internal configuration of the single guanine; we find that its main effect is to stabilize the structure, as proved by large calculated adsorption energy ($\Delta E = -810$ meV/G). On the other hand, H-bonding does not favor the lateral coupling of electron states between neighboring molecules. As shown in Figure 2b, where the charge density plot of the HOMO is presented, the ribbon states are localized around the single guanines, with no Bloch-type delocalization through the hydrogen-bonds. The density of states (DOS, top of Fig. 3a) shows isolated sharp peaks corresponding to the energy levels of G, and the energy bands (not shown here) are dispersionless. We thus conclude that band-like conductivity, through extended states, is not a viable mechanism for electron transport along the ribbon axis.

The picture changes drastically when we consider stacked configurations. In a previous work [18], we demonstrated that the electronic properties of vertical stacks of G molecules are very sensitive to the $\pi - \pi$ coupling: A strong $\pi - \pi$ superposition is mandatory to

have a Bloch-like conduction along the stacking direction. Here, we present a stacked configuration of planar ribbons, where the stacking direction is orthogonal to the plane of the ribbon. Even though experimental results prove that the ribbons self-organize in fibers [3], the X-ray structure of single crystal is still missing, therefore the real stacking geometry is unknown. We report our results for a configuration in which the ribbons are perfectly eclipsed one above each other and the band dispersion is expected to be maximized. In this configuration, we investigated the concurrent effects of H-bonding in the ribbon plane and $\pi - \pi$ coupling along the stacking direction: a reduced value of the adsorption energy ($\Delta E = -310$ meV/G), with respect the isolated wire, is the index of electrostatic repulsion of $\pi - \pi$ superposition.

We then examined the electron states near the gap edge, that affect the conduction properties; these are π orbitals very sensitive to the vertical superposition. As an example, the LUMO of the eclipsed structure is shown in Fig. 2c: the $\pi - \pi$ coupling induces the formation of Bloch-type orbitals delocalized along stacking direction. On the other hand, as it happens for isolated ribbons, the electronic states are not extended in the plane, indicating that H-bonding gives negligible contribution to band conductivity. This is consistent with the bandstructure (Fig. 3b). The HOMO- and LUMO-derived bands are dispersive along the stacking direction ($\Gamma - A$); while they are almost flat along the ribbon axis ($\Gamma - X$). The calculated effective masses for electrons and holes are $m_e = 1.24$ and $m_h = 1.07$ (in units of the free electron mass) along the stacking direction, whereas they are very high along the axis of the ribbons. We conclude that the $\pi - \pi$ interaction enhances band properties, improving the mobility of the charge carriers only along the stacking direction. The DOS (bottom of Fig. 3a) for the eclipsed ribbons confirms this behavior, and shows wider ranges of allowed energies with respect to isolated ribbons, especially in the region around the gap. Band properties of fibers may be similar to those of inorganic wide-bandgap semiconductors (*e.g.* GaN, AlN [19]) for which Bloch conduction has been proved in presence of doping. Our results are in agreement with the experimental evidence of a semiconducting behavior of guanine ribbons.

In order to explain the rectifying properties of single nanocrystals, we must consider the polar nature of the G-ribbons. Due to the relative orientation of the single G's in the ribbons, molecular dipoles arrange to form a net dipole oriented along the ribbon axis (Fig. 1). The calculated values of dipoles, for finite sequences of 2 ($|\bar{\mu}| = 14.6$ D) and

4 ($|\bar{\mu}| = 32.8$ D) guanines, indicate that a dipole-dipole interaction arises along ribbons. The associated electric field may couple with proper Bloch-momentum of charge carriers, defining a different effective direction for electron transport. The presence of a favorite direction justify the diode-like character of experimental I-V curves.

In summary, we have demonstrated that supramolecular aggregates of guanines may form solid-state materials with interesting conduction properties. Ribbon fibers present wide-bandgap semiconducting behavior, compatible with Bloch-like conduction along stacking direction. A strong dipole field influences band properties of such nanocrystals, inducing preferential direction in movement of electron and holes, as confirmed by recent experimental results. [3].

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FIG. 1: Isolated planar guanine ribbon: Relaxed geometry, dipole moment and isosurface of total charge density. In the inset the relaxed geometry, the dipole moment and the isosurface of total charge density of a single guanine molecule are shown.

FIG. 2: a) Isosurface of the HOMO for the isolated G molecule; b) Isosurface of the HOMO for the planar guanine ribbon; c) Isosurface of the LUMO for stacked planar ribbons in the eclipsed configurations.

FIG. 3: a) Density of States (DOS) for isolated (top) and stacked (bottom) planar ribbons; b) Bandstructure for stacked planar ribbons in the eclipsed configuration.

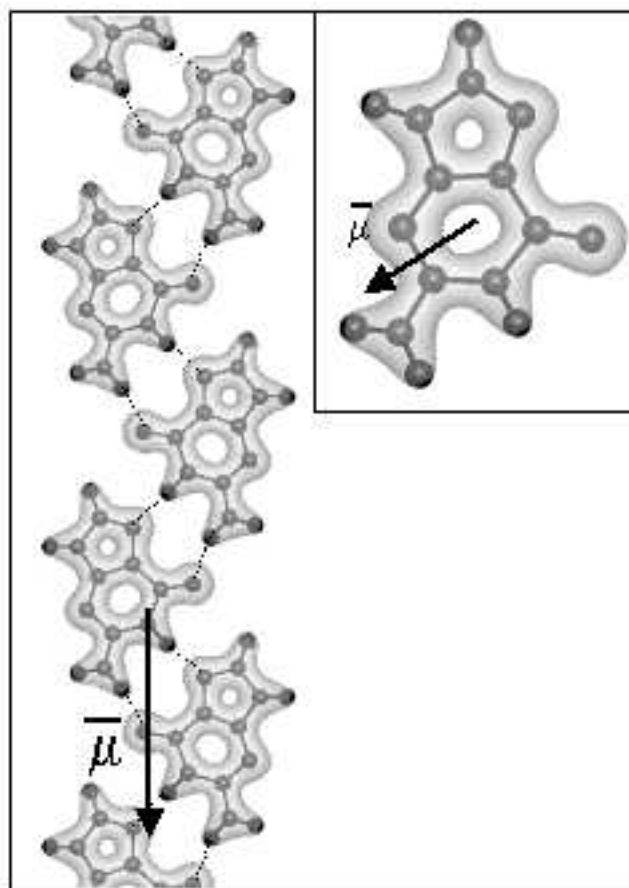


Fig. 1
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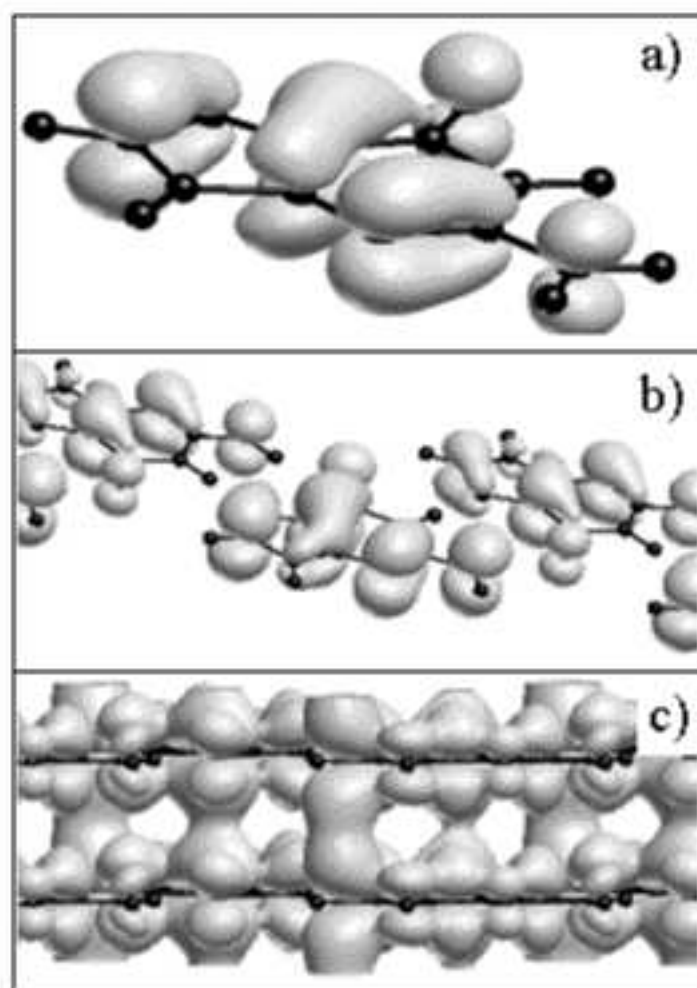


Fig. 2
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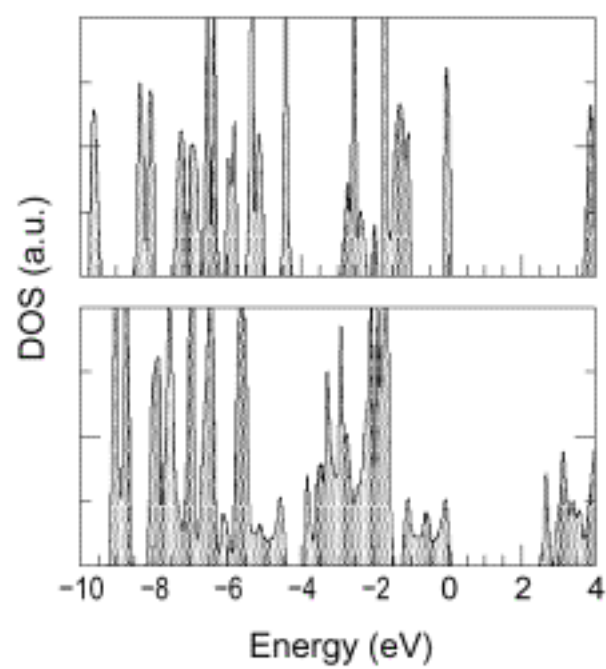


Fig. 3a

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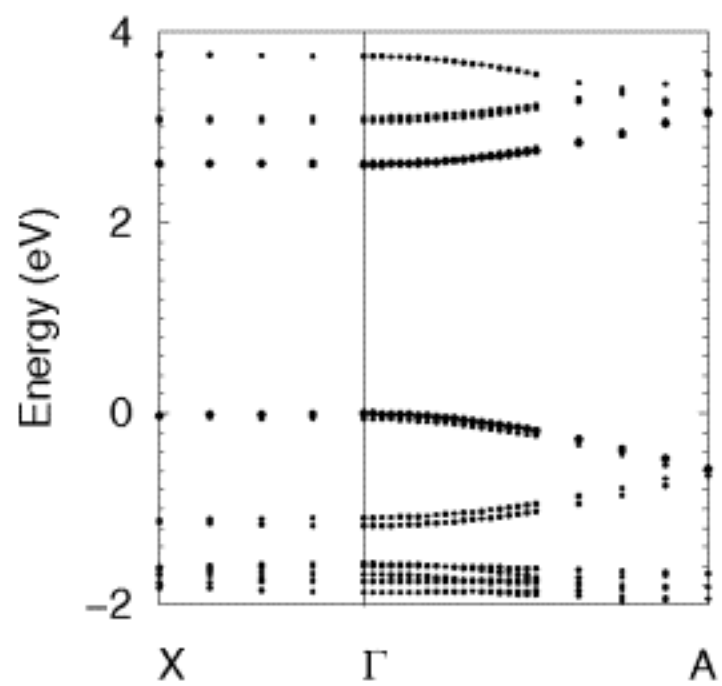


Fig. 3b

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